

## THE ASSOCIATED OCCURRENCE OF THREE ZnS MODIFICATIONS IN GYÖNGYÖSOROSZI

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In the subvulcanic veins of the miocen pyroxene andesites of *Gyöngyösoroszi* (Mátra-Mountains) among the ores sphalerite and galena dominate and to a smaller extent pyrite and chalcopyrite may be found too. The wurtzite occurring here in a striking variety is very interesting from a mineralogical point of view. The wurtzite occurs in epithermal veins rich in quartz, characteristically banded and produced by residual solutions rich in volatile substances. In Hungary this mineral is so far only known to occur in this mine.

As has been reported [1] in the *Acta Mineralogica Petrographica* Tomus VII. 1953/54 in the course of the exploitation in 1951 wurtzite samples were already found at the *Károly*-level of the *Károly*-vein. The radial fanlike wurtzite crystal aggregates which were still then rare occurrences formed 0,5—1,5 cm broad bands and band rows devided by thin quartz layers in the banded quartz of the ore-vein. These wurtzite crystal aggregates always contained as inclusions larger quantities of chalcopyrite blades. The copper content of the analysed wurtzite crystal aggregates amounted to 0,88—1 per cent. It was already then conspicuous that sphalerite crystals were deposited oriented on the fanlike extremely finely threaded wurtzite aggregates. The threefold axis of the sphalerite tetrahedrons always ran parallel with the *c* crystallographic axis of the wurtzite threads. Photomicrographs of these oriented wurtzite — sphalerite intergrowths were also published.

In the veins of *Gyöngyösoroszi* systematic mining goes on since then and in its course larger amounts of wurtzite have been found. The paragenetic morphologic optical and chemical examinations of the recently discovered wurtzite samples were made in our institute, however, as owing to pecuniary reasons unfortunately we have not got equipment for X-ray examinations these were carried out at my request in Budapest by K. Sasvári [2]. The referring results are published on page 23. of this volume.

The main ore-vein of wurtzite is the *Károly*-vein, its ore contains the most wurtzite. Its crystal aggregates occur on the 200th level in thin veinlets, in the southern drift of the 100th level and on the 50th

level also thin band rows decided by thin quartz gangue. These wurtzites separated previously towards the border of the vein from solutions of higher temperatures and always contained chalcopyrite inclusions. Twenty meters below the Károly-level this older wurtzite occurs too, but beside it in the middle of the ore-vein younger wurtzite may also be found. This typical dark brown »Strahlenblende« sometimes being 5 cm thickness consisting of the radial aggregates of conically diverging fine threads is deposited on coarsely granulated galena, galena-sphalerite or quartzous vein filling. Its surface projecting into the narrow cavity which extends in the middle of the ore-vein is glaskopflike slightly convex and has greasy luster. The conic bundles consisting of fine wurtzite threads sometimes ends on the surface in badly defined hexagons. Small transparent brown sphalerite crystals with adamantine luster are oriented overgrown on the surface of the hexagons. The sphalerite crystals one mm in size are the combinations of the forms

(111)

( $\bar{1}\bar{1}1$ )

(100)

and are overgrown with one of the plates of the dominating tetrahedron onto the (0001) plates of the wurtzite bundles. Beside the sphalerite crystals younger pyrite more rarely galena hexahedrons a few mm in diameter can be found.

The »Strahlenblende« is in thin sections transparent with a light brown mildly brownish yellow colour, its pelochroism is hardly visible, however, its anisotropy is significant. The cleavage of the wurtzite

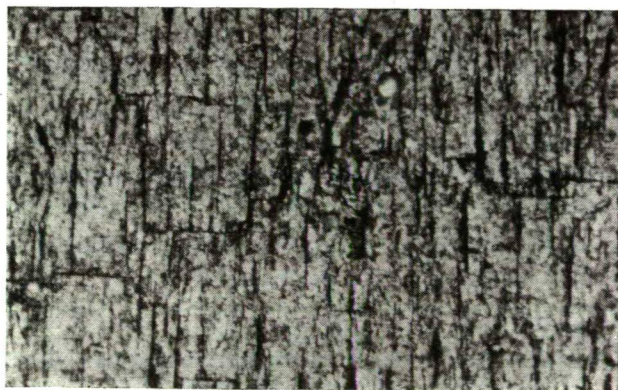


Fig. 1. Thin section of wurtzite. Excellent may be seen the cleavage directions perpendicular to each other. Parallel nicols.  $\times 160$ .

threads forming the conic bundles takes place in two directions perpendicular to each other, their extinction is parallel. (Fig. 1.) The whole bulk of the substance consists of wurtzite none of which was transformed into sphalerite. In the thin sections in which sphalerite may also be detected the two varieties differentiate in colour and cleavage sharply from each other proving that the sphalerite formed as sphalerite and is

not paramorph after wurtzite. (Fig. 2.) In some of the sections the sphalerite contains many chalcopyrite inclusions, however, the wurtzite does not contain any.



Fig. 2. Wurtzite and sphalerite side by side. It is well visible the difference between them in colour and cleavage directions. Parallel nicols.  $\times 160$ .

According to the X-ray examinations and personal communications of K. Sasvári this »Strahlenblende« is normal 2H wurtzite. Its chemical composition is on the basis of the analysis as follows:

Zn	61,69 per cent
Fe	4,64
S	33,36
SiO <sub>2</sub>	0,63
	<hr/>
	100,32 per cent

Analysed by Mrs. Eve Klivényi

By courtesy of Mrs. M. Földvári this and the following samples were spectrographically examined in the Laboratory of the State Geological Institute. The »Strahlenblende« contains

in significant traces	Pb	Cu
in traces	Cd	
in weak traces	Mn	

Far more rarely than the latter a black coarsely radial occasionally even 3—5 cm thick »Strahlenblende« occurs at 3675 m in the adit of the

western part of the mineralised region. In the intermediate spaces of the fibrous wurtzite aggregates one can find longitudinal small cavities following the direction of the *c* crystallographic axis, their structure looser and their walls are covered with sphalerite crystals overgrown oriented on the wurtzite fibers. These crystals are mostly polysynthetic spinel-twins, sometimes — more rarely — simple tetrahedrons, the three-fold axis of the crystals runs parallel to the *c* crystallographic axis of the wurtzite threads. Beside these sphalerite crystals having the same colour and being of the same age as wurtzite we find in the small cavities brown transparent octahedral sphalerite crystals not oriented overgrown and tiny pyrite pentagonal dodecahedrons with lustrous planes which formed later.

Moreover pyrite can be found associated with coarsely granular galena, or alone, in the lower concave and upper convex surfaces of the layer of this black »Strahlenblende«. Where the surface is not covered by pyrite and galena the hexagonal boundaries of the wurtzite crystal aggregates are well visible. In thin sections this red brownish transparent anisotropic wurtzite contains far more Fe than the former owing to its dark colour its pleochroism is considerably weaker than could be expected, the extinction of the fibers is parallel. In the case of this wurtzite containing more Fe a part of the substance has already transformed into sphalerite but it has kept a cleavage resembling that of wurtzite thus it is paramorph after wurtzite. It seems of interest that the wurtzite containing more iron transformed partly into sphalerite and not — as stated by *Ehrenberg* — the one containing the smaller amount of iron.

The result of the chemical analysis of the black »Strahlenblende«:

Zn	58,19 per cent
Fe	7,74
S	32,92
SiO <sub>2</sub>	1,20
	<hr/> 100,05 per cent

Analysed by *Mrs. Eve Klivényi*.

#### Demonstrated spectrographically

in significant traces	Cd	Pb	Cu
in traces	Sn		
in weak traces	Mn		

The most interesting wurtzite occurrence was found on the 100th level of the Károly-vein, about 80—90 m from the pit.

In the granular quartz of the vein a brown 1—2,5 cm broad frost-worklike wurtzite band extends over scattered galena patches. Over it there extends a 6—8 cm thick finely granular quartz layer with scattered pyrite and then again a thin finely threaded wurtzite band which goes over into scattered ZnS crystal aggregates and crystals intergrown in quartz. (Fig. 3.) Towards the middle of the ore vein on the side of the sample opening into a small cavity calcite is deposited on the quartz and intergrown into this calcite many crystal bundles, small crystals associated



with little quartz crystals and kaolin occur. As a substance filling up the cavities kaolin plays a considerable role in the mineral associations.

By dissolving the crystals cautiously with dilute HCl black pyramids were obtained. The lower part of the steep pyramids one mm in size are delimited by the larger always slightly convex plane  $000\bar{1}$  showing a greasy lustre. Frequently, as will be described later this plane did not develop. On the top  $0001$  does altogether not occur, or if it does it is small concave and has a dull greasy lustre. The planes of the pyramids are concavely curved and striated in a horizontal direction. The planes give extremely weak reflection series thus they cannot be measured.



Fig. 3. Crystal aggregates of  $\beta'$ -ZnS-3R in quartz. Parallel nicols.  $\times 100$ .

The pyramids are not monocrystals, but mainly tentlike aggregates of small columnar crystals extending in a longitudinal direction. The orientation of the  $c$  crystallographic axis of the small crystals scatters within an  $\pm 5-7^\circ$  angle. Frequently the interior of the pyramidal crystal aggregate is empty, the middle of the plane  $000\bar{1}$  is hollow. (Fig. 4.) Still more often the single crystals of which the crystal aggregate is built up overgrown one another, their length varies and plane  $000\bar{1}$  does not develop at all, the end of the crystal is broomlike. (Fig. 5.) The crystal aggregate sometimes consists of smaller, steep, pyramidal crystal aggregates too and occasionally of the small crystals described bellow. According to the examination of K. Sasváry the crystals are  $\beta'$ -ZnS-3R variations.

The crystal aggregates showing the form of a pyramid are 1—3 mm long, in a thin section they show a brownish-yellow colour, they are transparent and anisotropic, their extinction is owing to the radial situation of the small crystals of which they are built up undulating.

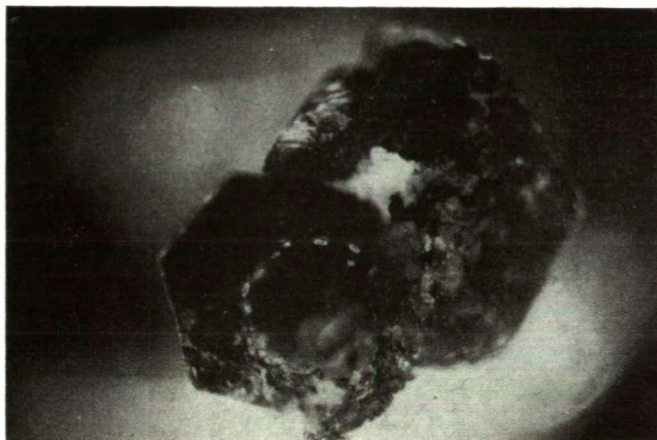


Fig. 4. The hollow  $0001^-$  planes of the pyramidal crystal aggregates of  $\beta'$ -ZnS-3R. Parallel nicols.  $\times 80$ .

Both these crystal aggregates and the »Strahlenblende«s mentioned above fail to show any luminiscence phenomenon which may be the result of their dark colour due to their great Fe content.

The results of analyses carried out on samples of selected pyramidal crystal aggregates are

Zn	61,70 per cent
Fe	5,10
S	33,22
	<hr/>
	100,02 per cent

Analysed by Mrs. Eve Klivényi

#### Demonstrated spectroscopically

in significant traces	Pb
in traces	Cd
in weak traces	Sn

It is striking that in the wurtzite from Gyöngyösoroszi Cd is only contained in traces or even only in weak traces.

The  $\beta'$ -ZnS-3R small crystals building up pyramidal crystal aggregates are 1—1,4 mm long, straw-wine-yellow coloured, transparent and translucent. They vary to a great extent as there are among them 1. fully consisting of  $\beta'$ -ZnS-3R variety showing pronounced anisotropy, 2. the greater part consisting of  $\beta'$ -ZnS-3R to which as oriented intergrowth sphalerite is associated and 3. small crystals principally consisting of sphalerite.

The  $\beta'$ -ZnS-3R crystals are without exception elongated in the direction of the  $c$  crystallographic axis, their dominating crystal shape is the hexagonal prism, the sphalerite always appears in polysynthetic spinel-twin crystals the twin individuals are usually very thin lamellae.

In the simplest case the small crystal has a curved plane and is thin sometimes quite dripstonelike, or a very steep pyramid or slender hexagonal prism. The surface of the dripstonelike ones is unequal and dull, that of the others has an adamantine lustre their colour is light straw-wine-yellow they are entirely anisotrope and their substance is  $\beta'$ -ZnS-3R (Fig. 6.).

Besides simple  $\beta'$ -ZnS-3R crystals other samples showing oriented intergrowth also occur among the crystals the whole substance of which is anisotrope. Thus in the case of the crystal illustrated on Fig. 7. there protrudes out of plane 0001 a frequently-varying combination of prisms and pyramids getting always thinner and from which a steep pyramid with a slightly curved plane taking up the shape of a prism emerges. The small crystal is covered by the thin 0001 plane. On a crystal fragment — Fig. 8. — an oriented intergrowth of a prism-pyramid tapering upwards continually can be seen. At the second crystal type the  $\beta'$ -ZnS-3R intergrows with sphalerite in an oriented manner. This type reminds one of the crystal groups intergrown in an oriented manner produced sublimatively by Lorenz's method described in 1954 by R. Mitchell and A. Corey [4]. Whilst in their case on each of the  $\pm$  tetrahedron planes — also in the case of spinel-twins — a wurtzite prism is overgrown on the crystals from Gyöngyösoroszi always only one  $\beta'$ -ZnS 3R prism may be found the crystallographic axis  $c$  of which runs parallel

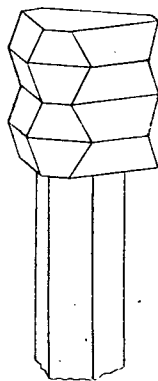


Fig. 9. Drawing of sphalerite spinel-twins oriented grown on the prism of  $\beta'$ -ZnS-3R.

with the threefold axis of the polysynthetic spinel-twin of the sphalerite crystals. (Fig. 9.) This is quasi the »handle« of the whole crystal group oriented intergrown. This »handle« proceeds sometimes on the plane of the tetrahedron covering the polysynthetic sphalerite crystal group, (Fig. 10—11.) even on the photomicrograph prepared under crossed nicols

it is well visible that the anisotropic »handle« goes through the strongly distorted isotropic sphalerite twin crystals. (Fig. 12.) In this case therefore the younger sphalerite has grown oriented onto the  $\beta'$ -ZnS-3R crystal.

The sphalerite parallel grown is always a polysynthetic twin lamellae row flattened in the direction of the threefold axis running parallel to the  $c$  crystallographic axis of the  $\beta'$ -ZnS-3R crystal.

It is known that the common layer in the crystal network of the spinel-twin of the sphalerite shows a wurtzite structure. On some of the small crystals the polysynthetic twin blades are so thin and follow each other so densely that optically the two ZnS varieties cannot be differentiated. It may be that the two varieties vary in very close fine layers, but possibly the anisotropic »handle« goes through the crystal and on this »handle« crystallized the extremely fine lamellar polysynthetic twin aggregate of sphalerite.

On Fig. 13. it seems as if a sphalerite »octahedron« were deposited on the anisotropic »handle«. Also in this case the sphalerite crystal is a polysynthetic twin, one can see the extremely fine twin lamellae, however, one twin individual is far better developed than the other. On this sample too it is well visible that the  $\beta'$ -ZnS-3R prism overgrows the sphalerite. The  $\beta'$ -ZnS-3R crystal showed on Fig. 14. is built up of prism-pyramid-prism and end in polysynthetic twins of sphalerite.

Finally there are crystal aggregates which are predominantly polysynthetic sphalerite twins and almost entirely isotropic only in some points one can see anisotropy shown by a weak extremely narrow layer (Fig. 15—17.).

Further examinations are in progress.

#### SUMMARY

In the subvulcanic epithermal Zn—Pb veins of *Gyöngyösoroszi* all three crystallized varieties of ZnS the  $\alpha$ -ZnS sphalerite, the  $\beta$ -ZnS-2H wurtzite and the  $\beta'$ -ZnS-3R occur one beside the other.

This is the only wurtzite occurrence in Hungary. The substance of the relatively frequently occurring »Strahlenblende« is normal 2H wurtzite. This is the first natural occurrence of the  $\beta'$ -ZnS. I suggest to give this variety the name of *mátraite* as it was first recognised in the veins of *Gyöngyösoroszi* situated in the *Mátra-Mountains*.

All three varieties of ZnS are primary minerals, *mátraite* is separated from acid solutions later than wurtzite at a lower temperature.

The small *mátraite* crystals one tenth of a mm in size are rarely composed completely of *mátraite*, usually they are crystal aggregates formed from the parallel intergrowth of *mátraite* and polysynthetic spinel-twins of sphalerite.



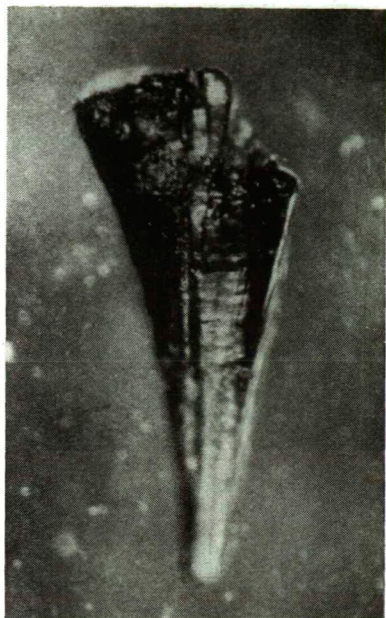


Fig. 5.

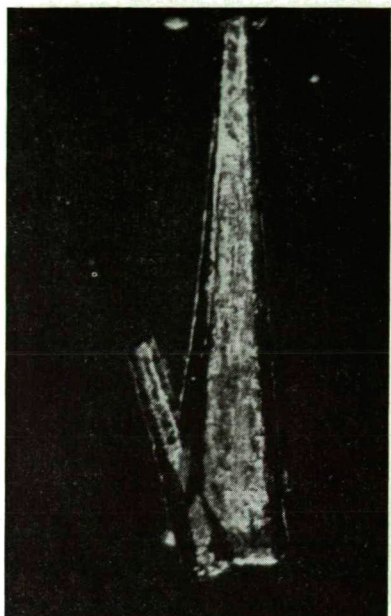


Fig. 6.

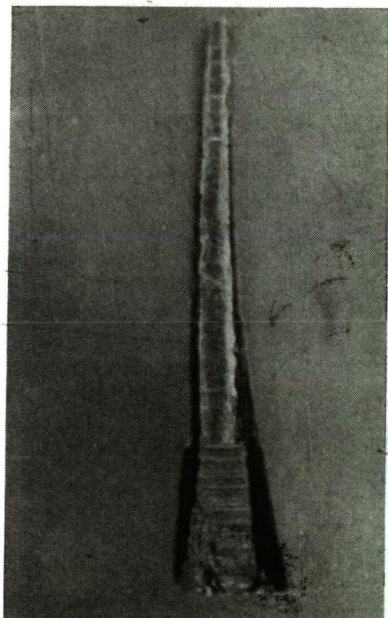


Fig. 7.

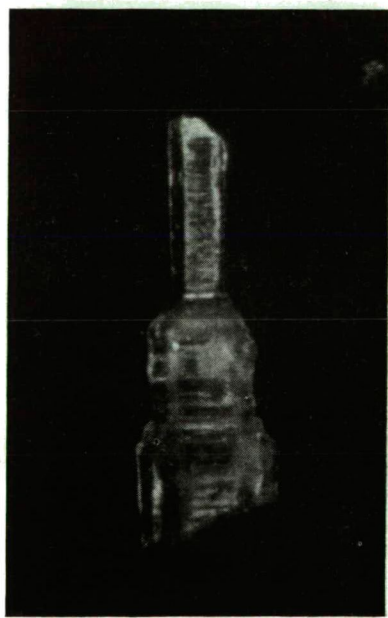


Fig. 8.

Plate II

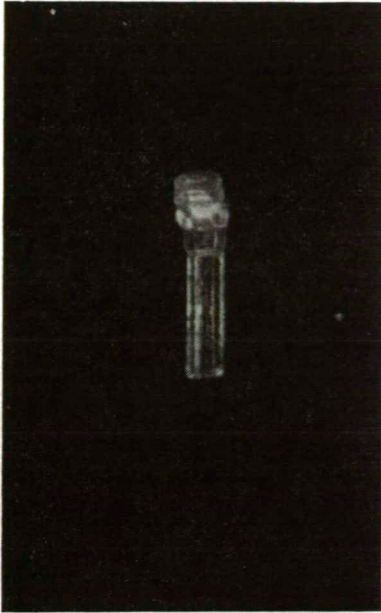


Fig. 10.

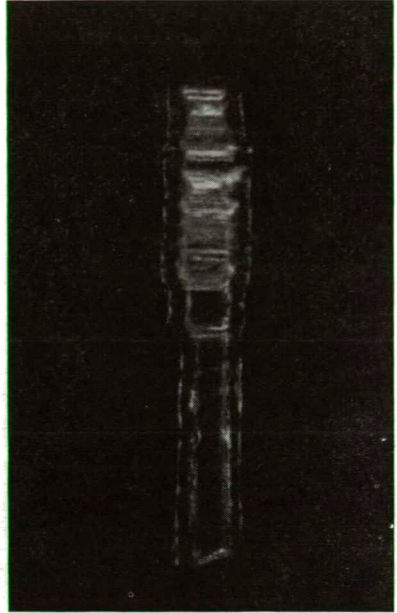


Fig. 11.

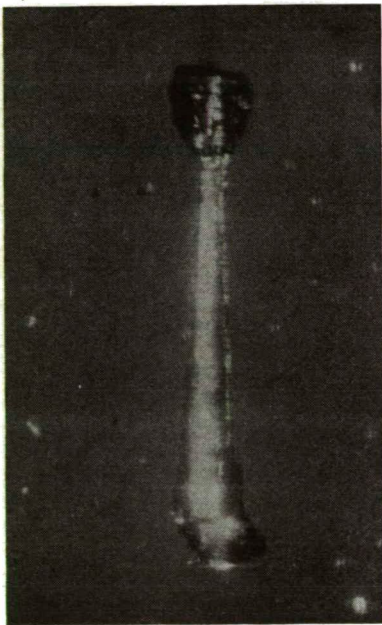


Fig. 12.

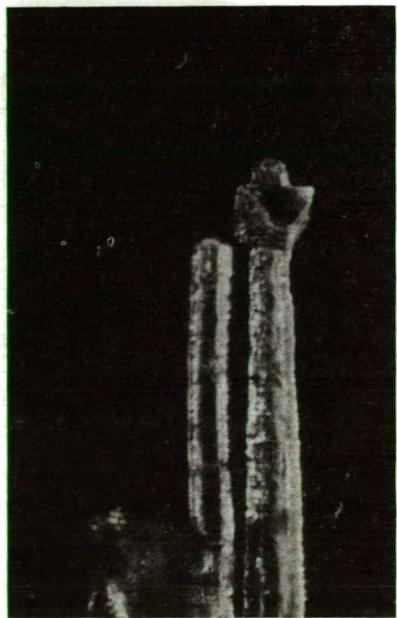
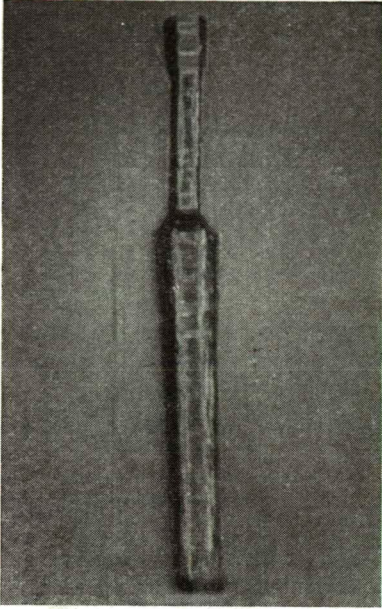
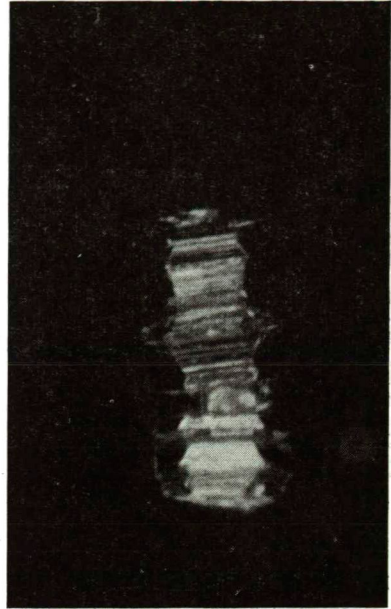


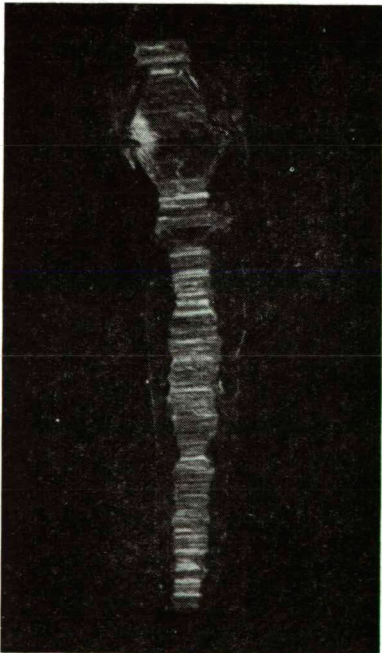
Fig. 13.



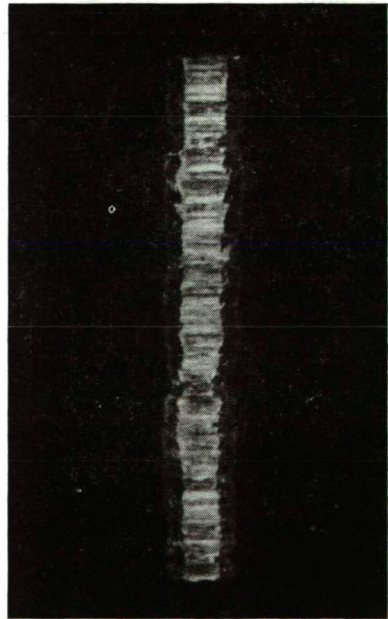
*Fig. 14.*



*Fig. 15.*



*Fig. 16.*



*Fig. 17.*

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## EXPLANATION OF THE PLATES

### Plate I

- Fig. 5. The broom-like opened end of the pyramidal crystal aggregates. Parallel nicols.  $\times 80$ .
- Fig. 6. Steep and pyramidal columnar crystal of  $\beta'$ -ZnS-3R. Parallel nicols.  $\times 70$ .
- Fig. 7.  $\beta'$ -ZnS-3R crystal. Parallel nicols.  $\times 75$ .
- Fig. 8.  $\beta'$ -ZnS-3R crystal oriented grown on. Parallel nicols.  $\times 150$ .

### Plate II

- Fig. 10. Polysynthetic spinel-twins of sphalerite oriented grown on  $\beta'$ -ZnS-3R crystal. Parallel nicols.  $\times 90$ .
- Fig. 11. Aggregate of sphalerite spinel-twins oriented grown on  $\beta'$ -ZnS-3R crystal. Parallel nicols.  $\times 120$ .
- Fig. 12. Sphalerite crystal deposited on the »handle» of the  $\beta'$ -ZnS-3R. Crossed nicols.  $\times 90$ .
- Fig. 13.  $\beta'$ -ZnS-3R penetrates the aggregate of sphalerite spinel-twins. Parallel nicols.  $\times 80$ .

### Plate III

- Fig. 14. Aggregate of sphalerite spinel-twins on the terminal end of  $\beta'$ -ZnS-3R crystal. Parallel nicols.  $\times 80$ .
- Fig. 15. Aggregate mostly consisting of sphalerite spinel-twins with portion of  $\beta'$ -ZnS-3R crystal. Parallel nicols.  $\times 120$ .
- Fig. 16. Aggregate of sphalerite spinel-twins. Parallel nicols.  $\times 100$ .
- Fig. 17. Aggregate of sphalerite spinel-twins presumably with portion of  $\beta'$ -ZnS-3R. Parallel nicols.  $\times 140$ .